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"Configurational Properties of a Stiff-Chain Diaryl Substituted
Polysilane in Dilute Solution"

by
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Dilute solution properties of a diaryl substituted polysilane indicate that the chain exhibits substantial stiffness in solution, with a persistence length on the order of 100Å. Measurements of the mean square radius of gyration, intrinsic viscosity and hydrodynamic radius at infinite dilution for a series of molecular weights were fit to theoretical expressions for the wormlike chain to estimate the persistence length. This large persistence length is consistent with the long wavelengths (395 nm) electronic absorption maximum observed for the diaryl substituted silanes. Results are compared with those reported previously for diaryl substituted polysilanes.

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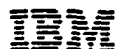All other editions are obsolete.

Research Report

CONFIGURATIONAL PROPERTIES OF A STIFF-CHAIN DIARYL SUBSTITUTED POLYSILANE IN DILUTE SOLUTION

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ABSTRACT: Dilute solution properties of a diaryl substituted polysilane indicate that the chain exhibits substantial stiffness in solution, with a persistence length on the order of 100Å. Measurements of the mean square radius of gyration, intrinsic viscosity and hydrodynamic radius at infinite dilution for a series of molecular weights were fit to theoretical expressions for the wormlike chain to estimate the persistence length. This large persistence length is consistent with the long wavelength (395 ± 10 nm) electronic absorption maximum observed for the diaryl substituted silanes. Results are compared with those reported previously for dialkyl substituted polysilanes.

INTRODUCTION

The equilibrium flexibility of a polymer chain backbone, *i.e.*, the case of rotation of the backbone bonds, has always been of great interest to polymer scientists. Silicon containing polymers present opportunities for investigation of configurational properties which are not available with more common carbon backbone polymers. Considering as a limiting case a completely unrestricted chain with all bond angles equally probable, consisting of n bonds of length ℓ, the mean square end-to-end distance $<r^2>$ is simply given by:

$$<r^2> = n\ell^2. \tag{1a}$$

Real polymer chains of fixed bond angles and restricted rotation have larger values of $<r^2>$ which may be expressed in a similar form:

$$<r^2> = n_k \ell_k^2 \tag{1b}$$

where n_k and ℓ_k are no longer the actual number of bonds and bond length but the number and length of larger imaginary bonds which yield the correct $<r^2>$ when treated as unrestricted.[1] The additional criterion necessary to define the Kuhn statistical segment length ℓ_k and n_k is that

$$L = n_k \ell_k$$

where L is the contour length or length of the fully extended chain. Adherence to Eq. 1b may be regarded as a definition of flexibility. Thus, chain molecules may be flexible despite considerable energy differences among rotational states of adjacent bonds. Larger hindrance to rotation necessitates larger values of ℓ_k, and thus the ratio of ℓ_k/ℓ may be used as a measure of chain flexibility. For example, typical synthetic organic polymers with carbon backbones have $\ell_k/\ell \simeq 10$. On the other hand, larger values of ℓ in the real chain can result in higher flexibility (ℓ_k/ℓ small) as is observed for poly(di-methylsiloxane) (PDMS). The increased bond length reduces steric hindrance to rotation. For highly hindered chains, as ℓ_k becomes very large, the number n_k of statistical segments becomes too small for Eq. 1b to be valid for molecular weights of interest, and these chains are regarded as stiff. As long as there is any flexibility in the chain, Eq. 1b will become valid at high enough molecular weight, but these molecular weights are often beyond those obtainable for stiff synthetic polymers.

EXPERIMENTAL

Intrinsic Viscosity

Dilute solution viscometry was carried out in toluene using a Cannon-Ubbelohde semi-micro dilution viscometer (size 25) in a temperature controlled bath (25.0 $\pm$ 0.2°C). At least three concentrations were measured and extrapolated to infinite dilution, using the Huggins and Kramers relations:

$$[\eta] = \eta_{sp}/c + k'[\eta]^2 c + ...$$
$$[\eta] = \ln \eta_{rel}/c + (k' - 1/2)[\eta]^2 c + ...$$

where $\eta_{rel} = t_{soln}/t_{solv}$ and $\eta_{sp} = \eta_{rel} - 1$ with t_{sol} and t_{solv} the efflux times of the solution and solvent, respectively. Values of η_{rel} varied from 1.2-1.6 and no kinetic energy correction was applied as $t_{solv} \geq 100$ sec.

Static Light Scattering

Measurements of the weight average molecular weight, M_w, the thermodynamic second virial coefficient A_2 and the z-averaged mean square radius of gyration $R_{G,z}^2$ were performed using a Chromatix KMX-6 low angle light scattering photometer and a Brookhaven BI200SM photogoniometer. Values of M_w and A_2 were obtained with the more precise KMX-6 from measurements at 4° scattering angle at several concentrations c:

$$\frac{K_c}{R_o} = \frac{1}{M_w} + 2A_2 c + ...$$

where the Rayleigh factor R_θ of 4° scattering angle was substituted for $R_o = R_{\theta \to o}$ without correction. The constant K is given by

$$K = \frac{4\pi^2 n^2 (dn/dc)^2}{N_A \lambda_o^4}$$

with n the refractive index of the solvent (1.497 for toluene), N_A Avogadro's number, λ_o the wavelength of the incident light (6328Å), and dn/dc the differential refractive index increment (0.131 ml/g). No corrections were made for anisotropy, as ρ_v at 0° scattering angle was found to be quite small ($\rho_v(0°) = 0.0044$ for sample 4-2).

with m the number of channels, 128. This criterion provides a larger number of points in the initial decay of the correlation function (for determination of Γ) at the expense of less precision in the second cumulant μ_2. The normalized second cumulant, μ_2/Γ^2, was 0.3 ± 0.1, consistent with the polydispersity of these samples. A representative correlation function is shown in Figure 2.

Size Exclusion Chromatrography

The molecular weight distribution of each sample was determined using Size Exclusion Chromatography (SEC). 150 μL of each sample at a concentration of 1-2 mg/mL was injected onto a set of 4 30 cm PLgel columns (porosity 10^6, 10^5, 10^4 and 10^3 Å) housed in a Waters 150C liquid chromatograph at 40°C. The mobile phase was tetrahydrofuran and the concentration detector was a differential refractometer. The column set was calibrated with a series of 15-20 narrow distribution polystyrene standards from Polymer Laboratories, and the data fit to a third order polynomial

$$\log M = A + Bt + Ct^2 + Dt^3$$

where t is the peak elution time of a PS standard of molecular weight M. Calculation of molecular weight averages relative to polystyrene was carried out with on IBM PCXT using software from Nelson Analytical. The chromatograms of all samples are displayed in Figure 3.

RESULTS AND DISCUSSION

Results obtained for all samples measured are listed in Table 1. No unusual behavior was observed in any of the measurements, and interpretation of the data was straightforward. All reported results (other than SEC) were obtained in toluene which was found to be a thermodynamically good solvent for the polymer. However, as discussed below, contribution of the excluded volume effect to the experimental parameters is expected to be small. A few measurements of M_w by light scattering were carried out in other solvents (tetrahydrofuran, hexane) and were found to be in agreement with results obtained in toluene. This result, and the consistency of results from the variety of techniques used, suggest that aggregation is not a problem for these solutions. Aggregation is often a contributing factor in solutions of stiff chain polymers, particularly those which can crystallize.

Estimation of the persistence length from the experimental data using the Kratky-Porod wormlike chain model requires correction for polydispersity effects. The unusual (and sometimes

poly(di-para-n-butylphenylsilane) samples measured here, $\alpha \leq 1.2$, so that the difference between the measured dimensions and those expected for θ conditions is at most 20%.

The most direct experimental assessment of the persistence length may be obtained from the root mean square radius of gyration measured by light scattering. The analytical expression for the unperturbed R_G^2 of a wormlike chain has been given by Benoit and Doty[5]

$$R_G^2 = (qL/3) - q^2 + (2q^3/L)[1 - (q/L)(1 - e^{-L/q})] . \tag{3}$$

The contour length L and molecular weight M are related by the mass per unit length M_L

$$M_L = \frac{M}{L} ,$$

also referred to as the shift factor. Although M_L as used in the wormlike chain model may not be exactly equivalent to the mass per unit length of the fully stretched chain,[2] we have used $M_L = 149 \text{Å}^{-1}$, determining L as the sum of the monomer unit projections on the backbone for a given M. This leaves only the persistence length q to be determined. A comparison of the experimental values ($R_{G,w}$) with the theoretical values (solid line) calculated from Eq. 3 with $q = 150 \text{Å}$ ($\ell_k = 2q = 300 \text{Å}$) and $M_L = 149 \text{Å}^{-1}$ is shown in Figure 4. The wormlike chain model appears to be a relatively good fit from the limited data. The theoretical line shows the curvature reflecting increased flexibility at higher M also seen in the experimental data. This would not be observed for a more flexible polymer in a good solvent, *e.g.*, the dihexyl substituted silane reported previously. A disadvantage in the use of R_G to estimate q is that R_G can only be measured for relatively high molecular weights with light scattering, so that the lower molecular weight region, where stiffness is more apparent and excluded volume effects minimized, is often inaccessible. The other disadvantage is that the R_G measured is a z-averaged quantity and is thus highly dependent on polydispersity, particularly on the high M portion of the distribution.

Estimation of q from hydrodynamic techniques such as intrinsic viscosity or diffusion requires an additional parameter, the hydrodynamic diameter or cross-section of the wormlike chain. This diameter d may be estimated from the partial specific volume $\bar{v}$,[6]

$$\bar{v} = (\pi N_A/4)(d^2/M_L)$$

polysilane, the <u>global</u> dimensions are approximated by a model wormlike chain with a persistence length of ~ 100Å. Thus, for the highest molecular weight studied, $L/q \cong 100$ and the chain dimensions are similar to those of a flexible model Kuhn chain with bond lengths $\ell_k \cong 200$Å, *i.e.*

$$R_G = \left[\frac{<r^2>_o}{6}\right]^{1/2} = \frac{n_k^{1/2}\ell k}{\sqrt{6}}$$

or 630Å. The experimental $R_{G,w} = 815$Å, in good agreement with the calculated value in view of the uncertainty due to polydispersity and excluded volume contributions. In contrast, the lowest molecular weight sample has $L/q < 1$, and may be treated as rodlike, *i.e.*

$$R_G = \left[\frac{L^2}{12}\right]^{1/2}$$

or 26Å. Although this R_G was too small to be measured by light scattering, it is consistent with the experimental $R_h = 20$Å. These approximate calculations illustrate the strong dependence of the geometry of the polymer chain on the molecular weight; particularly for $q \sim 100$Å. At low M the chain may be viewed as nearly rodlike, while at high M flexible chain behavior is observed. The diaryl substituted silanes provide a unique opportunity to investigate this range of backbone stiffness, with the degree of stiffness accessible to experimental investigation. Unlike many other stiff chain polymers in which the stiffness arises from long rigid groups in the backbone or from specific intramolecular interactions among backbone segments leading to a helical configuration, the stiffness in the diaryl substituted silane appears to be due only to unusually large energy differences among rotational states and should thus be very sensitive to changes in temperature. This is consistent with the rather large temperature dependence ($d \ln <r^2>/dT = -3.2 \times 10^{-3}K^{-1}$) observed for the di-n-hexylsilane.[17]

Table 1

Summary of Experimental Data

Sample	M_w^{LS}	$10^4 A_2^{LS}$	$R_{G,z}^{LS}(\text{Å})$	$R_{G,w}^{a)}(\text{Å})$	$R_h(\text{Å})$	$[\eta](ml/g)$	$M_w^{sec\ b}$	M_z/M_w
4-32	13,200	2.1	---	---	20	---	9500	1.2
4-2	49,000	1.0	265	67	50	17.7	41,000	10^c
64-2	450,000	3.3	592	334	292	169	506,000	2.6
75-2	546,000	---	609	428	268	---	193,000	1.8
67-2	1.8E6	2.6	1235	815	510	454	1.8E6	2.0

a. Calculated from $R_{G,z}^{LS}$ as described in text.
b. SEC weight averaged M relative to polystyrene.
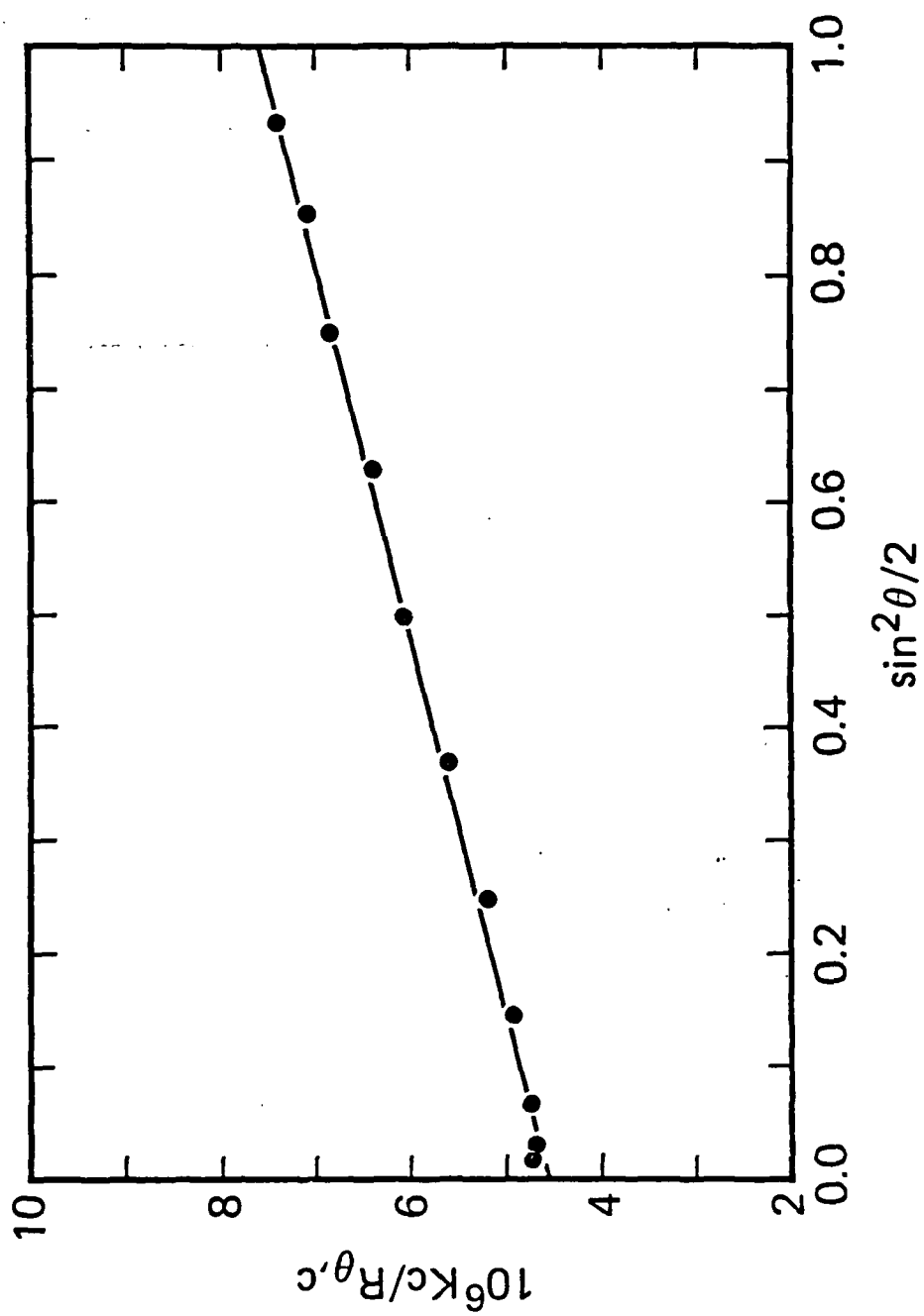c. This sample showed a high M tail, see Figure 3.

Figure 1. The angular dependence of $K_c/R_{\theta,c}$ for sample 64-2, with c = 1.58 mg/ml.
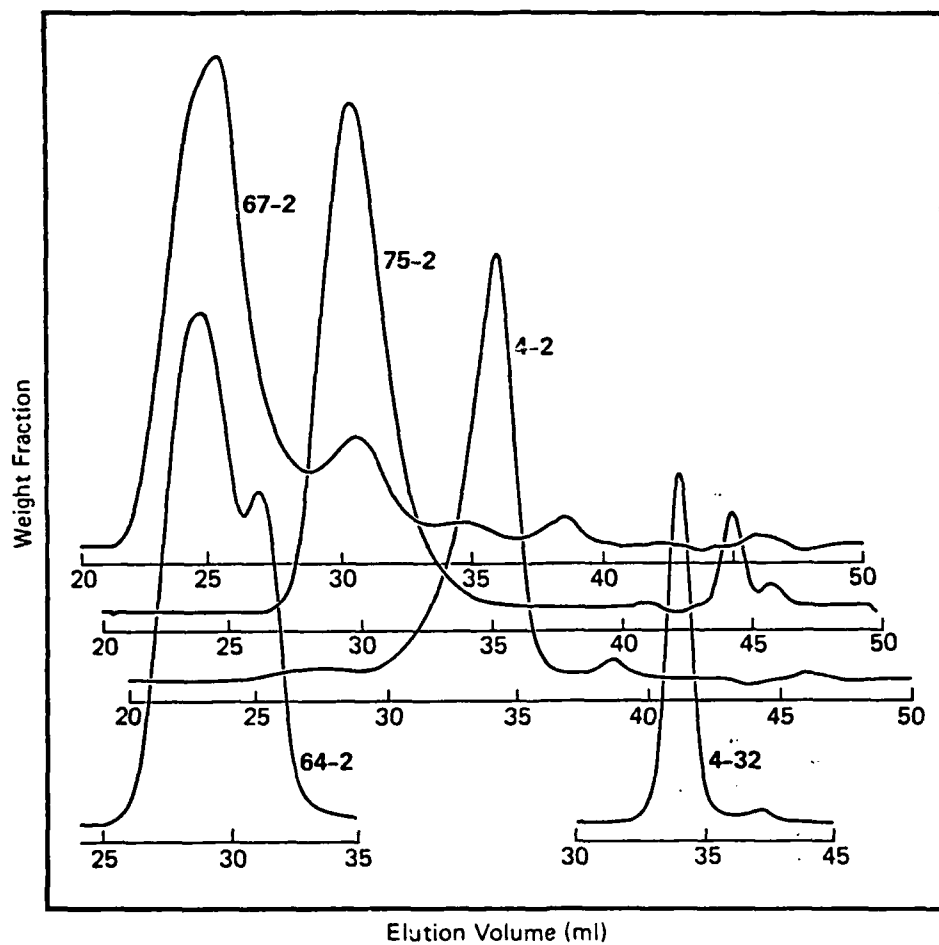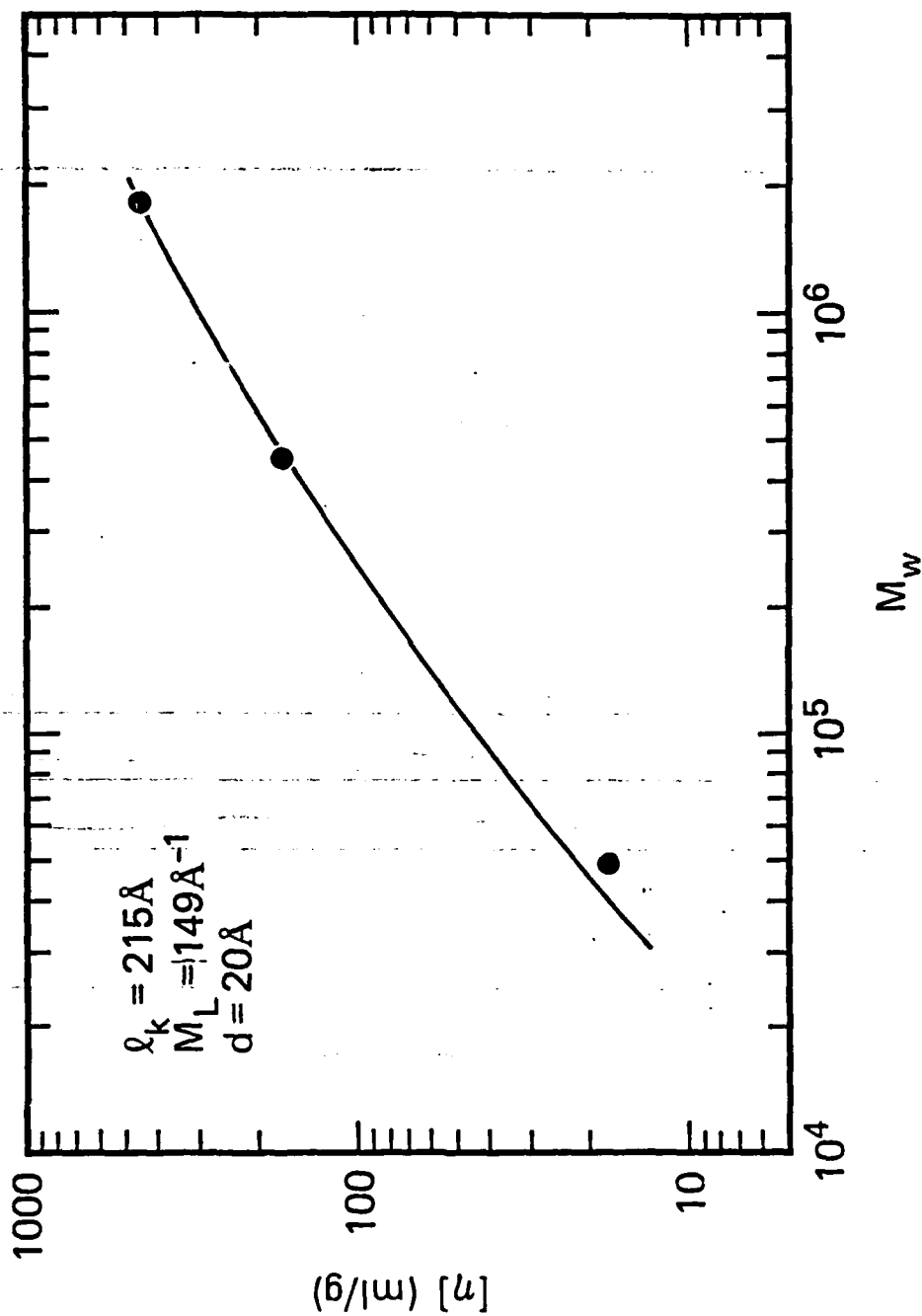
Figure 3. SEC chromatograms of the samples studied.

Figure 5. Comparison of measured values of $[\eta]$ with theoretical values (solid line) calculated with $q = 108\text{Å}$, $M_L = 149\text{Å}^{-1}$ and $d = 20\text{Å}$.